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**Abstract**

Constructed wetlands are increasingly used for water pollution treatment but may also be sources of the greenhouse gas $CH_4$. The effect of addition of two potential inhibitors of methanogenesis - iron ochre and gypsum - on net $CH_4$ emissions was investigated in a constructed wetland treating farm runoff in Scotland, UK. $CH_4$ fluxes from three 15-$m^2$ wetland plots were measured between January and July 2008 in large static chambers incorporating a tunable diode laser, with application of 5 t $ha^{-1}$ ochre and gypsum in May. $CH_4$ fluxes were also measured from control and ochre- and gypsum-treated wetland sediment cores incubated at constant and varying temperature in the laboratory. Ochre addition suppressed $CH_4$ emissions by 64±13% in the field plot and > 90% in laboratory incubations compared to controls. Gypsum application of 5 t $ha^{-1}$ in the field and laboratory experiments had no effect on $CH_4$ emissions, but application of 10 t $ha^{-1}$ to a sediment core reduced $CH_4$ emissions by 28%. Suppression of $CH_4$ emissions by ochre application to sediment cores also increased with temperature; the reduction relative to the control increased from 50% at 17.5 $^{\circ}$C to > 90% at 27.5 $^{\circ}$C. No significant changes in N removal or pH and potentially-toxic metal content of sediments as the result of inhibitor application were detected in the wetland during the study.

**Keywords:** constructed wetland; farm; gypsum; methane; ochre; pollution swapping

## 1. Introduction

$CH_4$ is the largest contributor after $CO_2$ to direct anthropogenic radiative forcing of the atmosphere, currently comprising 20% of direct forcing (IPCC, 2007), and is expected to contribute significantly to global warming and changes in atmospheric chemistry in the future. Natural wetlands are the single largest source of $CH_4$ globally, emitting 100-231 Tg $CH_4$ $y^{-1}$, with substantial emissions also occurring from rice agriculture (IPCC, 2007). Constructed

wetlands which mimic natural wetlands have been demonstrated to remove suspended solids, organic matter, N, P, potentially toxic metals, and pathogenic microorganisms from point and non-point source water pollution (e.g., Scholes et al., 1998; IWA, 2000; Hunt and Poach, 2001; Vymazal, 2007) and represent a promising technology for sustainable treatment of polluted water, including farmyard runoff (Carty et al., 2008). Such use of constructed wetlands for wastewater treatment may therefore result in 'pollution swapping' by increasing $CH_4$ emissions (Reay, 2004). Consequently, there is considerable interest in managing constructed wetlands, and also flooded rice fields, to minimise $CH_4$ emissions.

$CH_4$ emission from wetlands is the net outcome of $CH_4$ oxidation and production processes, the latter occurring as anaerobic microbial decomposition of organic material by methanogens, in particular de-carboxylation of acetate and reduction of $CO_2$ (Conrad, 1989). Decreases in $CH_4$ emissions measured after addition of $SO_4^{2-}$ and $Fe^{3+}$ to wetland soils (mainly in rice fields - e.g., van der Gon and Neue, 1994; Jäckel and Schnell, 2000; Ali et al., 2008, but also peatlands - e.g., Dise and Verry, 2001; Gauci et al., 2002) have been attributed to inhibition of methanogenesis, predominantly through stimulation of $SO_4^{2-}$ and $Fe^{3+}$ reducing bacteria which outcompete methanogens for acetate and hydrogen. Stimulation of $CH_4$ oxidation by $SO_4^{2-}$ (under anaerobic and aerobic conditions) and $Fe^{3+}$ addition (under anaerobic conditions) may also contribute to these observed decreases in $CH_4$ emissions (Kumaraswamy et al., 2001).

Gypsum is a $SO_4^{2-}$ source that is already widely used for improvement of agricultural soils and is the most common amendment for reclaiming sodic soils. A sustainable and cheap source of Fe is increasingly available in countries with a history of mining, such as the UK, in the form

of ‘ochre’ (i.e., $Fe(OH)_3$ and FeO(OH)), generated in large quantities by the precipitation of Fe in schemes to remediate drainage from abandoned mines. Although several possible uses of ochre have been identified, there is no large-scale outlet and it is often disposed of to landfill in the UK (Dobbie et al., 2009). However, ochre could be used in a more sustainable manner, by applying it to managed wetlands to stimulate $Fe^{3+}$ reducers and thereby reduce $CH_4$ production. Although $CH_4$ suppression arising from $SO_4^{2-}$ and $Fe^{3+}$ addition to wet soils has been widely demonstrated, the effect of ochre on $CH_4$ emissions has not been investigated. One concern with the use of ochre is the release of potentially toxic metals, which may also have been removed with Fe during mine water treatment. Furthermore, few studies with $CH_4$ inhibitors have been conducted in a temperate wetland environment and none in a constructed farm wetland. The aims of this study were to measure the effect of gypsum and ochre additions on $CH_4$ emissions from a constructed farm wetland and to evaluate the interaction between inhibitor application and temperature on $CH_4$ emissions.

## 2. Materials and methods

### 2.1 Study site and field experiment

The wetland studied was constructed in May 2004 to treat lightly contaminated water from a mixed beef and arable farm in south east Scotland (55°48' N, 2°13' E). The 0.9 ha wetland comprises five ponds separated by vegetated overland flow areas and receives field drainage, farmyard runoff and septic tank overflow via two inlets. In 2006-2007 N removal and $CH_4$ and $N_2O$ fluxes were monitored for the overland flow area between the first and second ponds (Reay and Paul, 2008; van de Weg et al., 2008). The same area was used for this study, in which, in

January 2008, three parallel plots (10 m x 1.5 m and 0.5 m apart) that exhibited uniform vegetation (dominated by *Holcus lanatus* grass), topography and hydrology were delineated by curved tunnels of 3-m long fibreglass canes.

The experimental design for both field plot and laboratory incubation studies was based on the before-after-control-impact-pairs method widely used in ecological studies (e.g., Carpenter, 1990). $CH_4$ fluxes were determined using 'mega-chambers' created on each measurement occasion by covering the fibreglass canes at each plot with a gas-impermeable highly reflective sheet, to minimise super-ambient heating, which was sealed around its bottom edge with lengths of heavy chain. The effectiveness of this closure technique had been demonstrated previously in identical mega-chambers at the site by measuring the linearity of $CH_4$ accumulation and dilution of $SF_6$ (Reay and Paul, 2008). $CH_4$ concentration in each mega-chamber was measured as a 5-s average using a tunable diode laser (Gas Finder 2.0, Boreal Laser Inc., Canada, lower detection limit 0.1 ppm at 10 m path length) connected to a laptop. A chamber closure period of 15 min was used and $CH_4$ flux rates were calculated from linear regression of accumulation curves. $CH_4$ fluxes were measured at around midday on six occasions between January and July 2008, three before and three after application of the inhibitors. Triplicate $CH_4$ flux measurements were normally made at each plot, with 5-min manual flushing between enclosures, apart from on 31 January 2008 when single measurements were made. $CH_4$ production and oxidation rates were not measured as net $CH_4$ flux was the key variable of interest in this study. Water pH and temperature was measured using hand-held probes in surface water overlying each field plot on every measurement occasion. From mid March 2008 water temperature was also measured every 5 s using a HOBO Pendant Temperature Logger installed below the water surface in between the

plots. The central plot was designated the control (no treatment). On 8 May 2008, after $CH_4$ flux measurement, 5 t $ha^{-1}$ of either ochre or gypsum was applied to the other plots following the methods of previous field studies using gypsum. Gypsum granules (diameter 2-5 mm, moisture content < 1.5%, Rootwise Ltd., North Yorkshire, UK) and ochre pellets (diameter 6.4-9.5 mm), made from a mixture of dried ochre, organic and inorganic binders, pelletizing aids and 5% by weight of water, were used. Laboratory solubility tests found that gypsum granules dissolved completely after 62 d but ochre pellets were still intact after 6 months submerged in deionised water.

2.2 Water and sediment sampling and analysis

Measurements of N removal by the wetland were not designed specifically to assess the effect of treatment, but formed part of the long-term monitoring of the wetland since 2006. $NO_3$ and $NH_4$ concentrations were determined by automated colorimetry using standard methods (Autoanalyser II, Bran+Luebbe, Norderstedt, Germany) in water samples collected every 2 wk at the wetland inlets and outlet. Potentially toxic metals and pH were measured in three separate sediment samples collected from each plot on 2 March 2008 before treatment and on 3 July 2008, approximately two months after treatment. The samples were collected using a stainless steel hand corer with a plastic liner (diameter 48 mm, length 0.51 m, Wildco, Buffalo, NY, USA), transported to the laboratory at 4 $^{\circ}$C and homogenised by hand before analysis. pH was determined with a calibrated hand-held probe in a slurry of 25 g fresh sediment mixed with 50 mL deionised water that had been stirred, left for 30 min and then re-stirred. Available potentially toxic metals (Al, As, Cd, Cu, Fe, Mn, Ni, Pb, Zn) were determined by ICP-OES (Perkin Elmer 5300DV Optima, Waltham, Massachusetts, USA) in filtered extracts prepared

within 24 h of sampling by shaking 5 g fresh sediment with 100 mL 2.5% acetic acid for 2 h. Total potentially toxic metals were determined by ICP-OES in digests of milled and ashed sediment prepared using HCl and $HNO_3$ (Allen et al., 1974). All sediment analyses were performed in duplicate and blanks were prepared.

2.3 Laboratory sediment core incubation experiments

Incubation experiments were conducted in a temperature-controlled water bath on pairs of sediment cores collected adjacent to the field plots in steel cylinders (diameter 0.18 m, height 0.12 m). The cores were sealed in plastic bags to minimise moisture loss and transported to the laboratory at 4 $^{\circ}$C where they were transferred to Perspex containers (diameter 0.19 m, height 0.40 m), each sealed with a lid equipped with gas sampling ports. Both containers were incubated for 4-7 d for acclimatisation (until measurable $CH_4$ emissions were detected from both cores) at the water temperature measured with the hand-held probe at the coring location immediately before the cores were taken. Gypsum or ochre was then applied to the surface of one of the cores, with the other serving as an untreated control. Because the cores were collected on five occasions between March and July 2008 the acclimatisation water temperature varied between experiments. Three experiments were conducted as follows. First, to identify the effect of inhibitor application on $CH_4$ emissions, pairs of cores were incubated at constant field water temperature for 6 d after treatment of one of the cores with ochre or gypsum at the same application dosage as the field plots (5 t $ha^{-1}$). In the second experiment a pair of cores was incubated at constant field water temperature as in the first experiment but a higher gypsum application dosage of 10 t $ha^{-1}$ was used for the treatment core. The third experiment, to examine the interaction between temperature and inhibitor application, was exactly the same as the first

experiment, apart from that after treatment the water temperature was increased in 5 $^{\circ}$C -steps, normally every 48 h. In all experiments the $CH_4$ flux from each core was determined three times a day from the change in headspace $CH_4$ concentration (3-h accumulation period on average), before and after flushing, measured using a Hewlett Packard 5890 series II gas chromatograph (Palo Alto, CA, USA) equipped with a flame ionisation detector (lower detection limit 0.01 ppm).

### 2.4 Data Analysis

All statistical analysis was conducted with Minitab v.15 using a significance level of $P < 0.05$. 1- and 2-way ANOVA followed by Tukey tests was used to compare $CH_4$ emissions before and after inhibitor application, and N removal (calculated as the % change on each sampling occasion in $NO_3$ and $NH_4$ concentrations between the wetland inlet and outlet water samples) between years and pH in surface water between field plots. Paired t-tests were used to assess whether any differences in pH and available and total potentially toxic metal concentrations in sediment between the field plots were affected by inhibitor application. The responses of $CH_4$ emission rates from the field plots and incubated sediment cores to temperature were determined by calculating $Q_{10}$ values. These indicate the increase in emission rate with a temperature increase of 10 °C and were calculated from the slopes of the $CH_4$ emission rates at different temperatures.

## 3. Results

### 3.1 Field experiment

$CH_4$ emissions from the field plots were positively related to water temperature, but were suppressed in the ochre plot after inhibitor application (Fig. 1). In the period before the application of inhibitors, there was no significant difference between the mean $CH_4$ emissions from the gypsum, control and ochre plots, these being 6.8, 5.2 and 5.3 mg $CH_4$ $m^{-2}$ $h^{-1}$, respectively. In the period after inhibitor application mean $CH_4$ emissions from the plots were significantly different ($P = 0.021$); the mean emission rate from the ochre plot of 9.0 mg $m^{-2}$ $h^{-1}$ was significantly lower than that from the control and gypsum plots of 27 and 28 mg $m^{-2}$ $h^{-1}$, respectively. This corresponded to a 64±13% reduction in $CH_4$ emitted from the ochre-treated plot compared to the control. There was no significant change in % removal of $NO_3$ ($P = 0.968$) and $NH_4$ ($P = 0.806$) in 2008 compared to 2006 and 2007 (Table 1), indicating that the ochre/gypsum applications did not appear to influence the N removal capacity of the wetland as a whole. Mean surface water pH was 6.9-7.1 in the plots before inhibitor application and 7.0-7.1 afterwards; it did not differ significantly between plots ($P = 0.906$) nor before and after treatment ($P = 0.773$). In addition there was no significant effect of inhibitor application on pH (6.9-7.2 before and 6.8-7.3 after) or concentrations of available and total potentially toxic metals in the field plot sediments. Although total Mn ($P = 0.033$) and available Ni ($P = 0.030$) sediment concentrations were significantly different after inhibitor application the increase occurred in all the plots.

**FIG. 1 AND TABLE 1 HERE**

3.2 Laboratory sediment core incubation experiments

In the experiments conducted under constant temperature conditions using the same 5 t $ha^{-1}$ inhibitor application dosage as in the field plots, ochre application resulted in a 90% reduction in $CH_4$ emissions compared to the control core only 5 d after application (Fig. 2a). There was no difference in $CH_4$ emissions between control and treatment cores after gypsum application (Fig. 2b) but, when a higher gypsum application dosage of 10 t $ha^{-1}$ was used (Fig. 2c), emissions from the gypsum-treated core were on average 28% lower than emissions from the control core. The large differences in $CH_4$ emission rates between control cores and the experiments probably result from the different core collection dates giving rise to different experimental incubation water temperatures and perhaps differences in activity of methanogenic organisms in the sediment cores (although microbial counts and activity measurements were not conducted). Figure 3 shows the $CH_4$ fluxes measured from the control and treatment (5 t $ha^{-1}$ inhibitor applications) sediment cores incubated at different temperatures. In the ochre experiment, $CH_4$ emissions from the two cores were similar in the acclimatisation period but, after treatment, $CH_4$ emissions from the control core increased more rapidly with temperature than emissions from the ochre core, before levelling off at 27.5 $^{\circ}$C (Fig. 3a). The extent of suppression of $CH_4$ emissions resulting from ochre addition increased with temperature, rising from about 50% at 17.5 $^{\circ}$C to > 90% at 27.5 $^{\circ}$C compared to the control core. In contrast, in the gypsum experiment, there was no apparent difference in $CH_4$ fluxes from the gypsum-treated and control cores at any of the incubation temperatures over the entire experiment (Fig. 3b).

**FIGS. 2 AND 3 HERE**

3.3 $CH_4$ emission-water temperature relationships

In the field experiment, $CH_4$ emissions from all three plots increased exponentially and significantly with water temperature between 3.5 $^{\circ}$C and 16.5 $^{\circ}$C (Table 2). However, the response of $CH_4$ emissions to temperature was less marked in the ochre plot compared to the control and gypsum plots. This effect was also apparent in the lower $Q_{10}$ value calculated for the ochre plot of 2.2 compared to 6.5 and 7.6 and for the gypsum and control plots, respectively. In the variable temperature sediment incubation experiments, $CH_4$ emissions increased either exponentially or linearly in all the incubated sediment cores for all the temperature ranges investigated, apart from the higher temperatures reached towards the end of the experiments. The diminished response of $CH_4$ emissions to temperature after ochre addition was also evident in these experiments as the $Q_{10}$ values for the ochre core were < 50% and < 20% those for the control core in the 12.5-22.5 $^{\circ}$C and 17.5-27.5 $^{\circ}$C temperature ranges, respectively. In contrast, in the gypsum treatment experiment $Q_{10}$ values for the treated and control cores were similar for the three temperature ranges tested.

**TABLE 2 HERE**

## 4. Discussion

The $CH_4$ fluxes measured in the field experiment were within the range of those determined from a constructed wetland in Finland receiving agricultural runoff and other constructed wetlands in northern Europe treating municipal wastewater (Søvik et al., 2006). $CH_4$ fluxes from the control and gypsum plots showed the same seasonal pattern, with low emissions in winter and higher emissions in summer as water temperatures increased. There was no significant

difference in $CH_4$ emissions between the field plots before treatment, but, after addition of inhibitors, $CH_4$ emissions from the ochre-treated plot were suppressed by 64% compared to the control plot during the 56-d post-treatment monitoring period. In sediment incubation experiments, $CH_4$ emission from the ochre-treated core was reduced by > 90% compared to the control core on the last day of the experiment. Similar reductions of 50-90% in $CH_4$ emissions have been reported after the addition of amorphous Fe(III) oxyhydroxide to tidal and freshwater river sediments (Lovley and Phillips, 1986). The expected mechanisms for decreased $CH_4$ emissions after ochre application are promotion of the activity of $Fe^{3+}$ reducing bacteria, resulting in a switch in electron flow from methanogenesis to $Fe^{3+}$ reduction (Frenzel et al., 1999) and/or increased $CH_4$ oxidation (Kumaraswamy et al., 2001). The incomplete suppression of $CH_4$ emissions after the addition of ochre to the field plot may have a number of causes, which need further investigation, including: the low solubility of ochre; application of ochre to the vegetated surface of the wetland without mixing to incorporate it throughout the sediment depth; the continued presence of oxic zones due to the flow of oxygenated water through the wetland; and the high organic matter content of the wetland sediment (25% loss on ignition after heating overnight at 500 $^{\circ}$C in a muffle furnace).

There was no change in $CH_4$ emissions compared to controls in either the field and laboratory experiments when gypsum was applied at 5 t $ha^{-1}$. However, at a higher gypsum application dosage of 10 t $ha^{-1}$ in the laboratory, there was evidence of some suppression of $CH_4$ emissions, indicating that $SO_4^{2-}$ additives may have the potential to limit $CH_4$ emissions in constructed wetlands. Further investigation is required to understand the apparent absence of $CH_4$ suppression after gypsum application to the study wetland, but the following explanation

may be suggested at this stage. The ratio of $SO_4^{2-}$ to organic matter in the wetland sediment may have been too low for the gypsum application to have any effect as $SO_4^{2-}$ reducers can only out-compete methanogens for organic carbon if $SO_4^{2-}$ is in excess (van Bodegom and Stams, 1999). Reductions in $CH_4$ emissions reported after gypsum application at lower dosages than used in this study (for example, 1-2 t $ha^{-1}$ to rice fields reduced $CH_4$ emissions by 29-46% (Lindau et al., 1994)) could have occurred because these agricultural soils have a sufficiently high ratio of $SO_4^{2-}$ to organic matter for methanogens to be suppressed. This explanation is supported by studies which showed that organic matter addition to rice fields resulted in increased $CH_4$ emissions (Schütz et al., 1989; Wassmann et al., 2000).

The $Q_{10}$ values for the field experiment indicate a strong response of $CH_4$ emissions to water temperature and are of similar magnitude to values of 2.7-7.9 derived from reported $CH_4$ emissions from peatlands in Minnesota, USA (Dise et al., 1993). The lower $Q_{10}$ for the ochre-treated plot could be indicative of the greater activity of $Fe^{3+}$ reducers after ochre application since a lower $Q_{10}$ value for Fe reduction than $CH_4$ production has been reported for rice field soils (Roden, 2003). Whilst the variable temperature sediment incubation experiment was conducted at higher water temperatures than at the field site it does indicate how suppression of $CH_4$ emissions from wetlands by inhibitors may respond to changing temperatures.

## 5. Conclusions

Application of the ochre pellets used in this study at 5 t $ha^{-1}$ would be anticipated to suppress $CH_4$ emissions from temperate constructed farm wetlands for at least 6 months, since the pellet

dissolution rate is > 6 months. There was no apparent increase in potentially toxic metals or pH change in sediment or change of N removal capacity of the wetland arising from application of ochre. Hence ochre pellets appear to be a suitable material for mitigating $CH_4$ emissions from constructed farm wetlands, thereby reducing the risk of pollution swapping and providing an additional benefit through use of a waste material which would otherwise have been landfilled. The results indicate that gypsum addition may also reduce $CH_4$ emissions from temperate constructed farm wetlands, but probably at higher application dosages. Further laboratory and field experiments are required to optimise the gypsum application dosage and examine its environmental acceptability before widespread application of gypsum to constructed wetlands can proceed. These studies should also seek to elucidate the mechanisms responsible for the reduction of $CH_4$ emissions from constructed wetlands by including killed control laboratory experiments and measurements of $SO_4^{2-}$ and Fe species and the activities of different bacterial communities in wetland sediment and water before and after inhibitor application.

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Fig. 1. Mean $CH_4$ flux (± standard error, where n = 3) and water temperature for the field plots on each measurement occasion. The January water temperature was the mean of measurements made at each plot using the hand-held probe. Thereafter, the water temperature is the mean of the values measured by the logger for the period of $CH_4$ measurements (3-4 h). The vertical arrow represents the application of inhibitors after 8 May measurements.

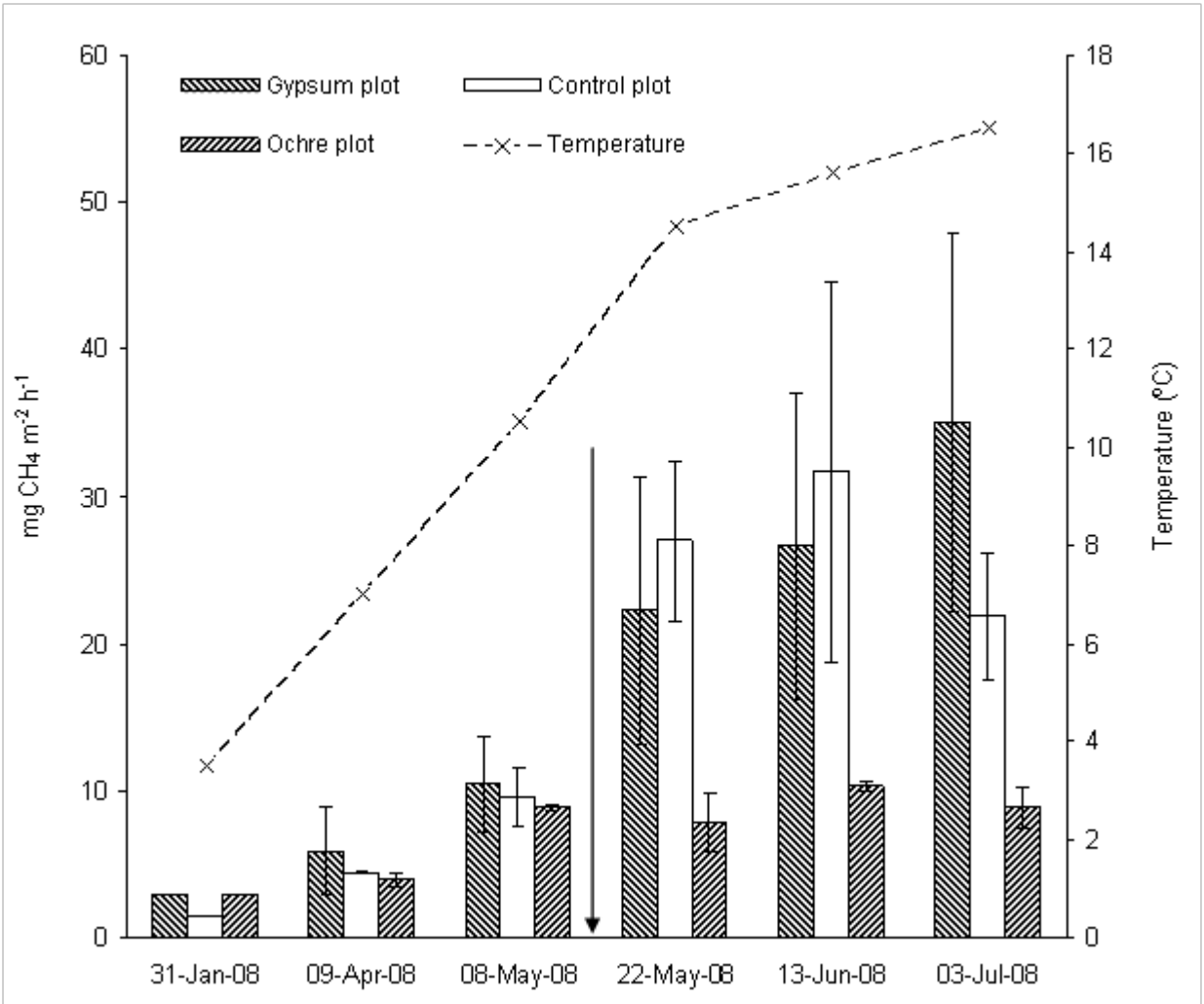

Fig. 2. Mean daily $CH_4$ fluxes (± standard error, n = 3 measurements per day) from pairs of sediment cores incubated at constant temperature with different treatments (a) ochre (cores collected 8 April 2008, water temperature 7.5 $^{o}$C, application rate 5 t ha$^{-1}$), (b) gypsum (cores collected 14 June 2008, water temperature 11.5 $^{o}$C, application rate 5 t ha$^{-1}$), (c) 'high' gypsum (cores collected 3 July 2008, water temperature 13.5 $^{o}$C, application rate 10 t ha$^{-1}$). Negligible $CH_4$ fluxes were measured at the start of the acclimatisation period which is represented by negative days. Inhibitor application to one of the cores occurred on Day 0 approximately 3 h before the first headspace $CH_4$ sampling.

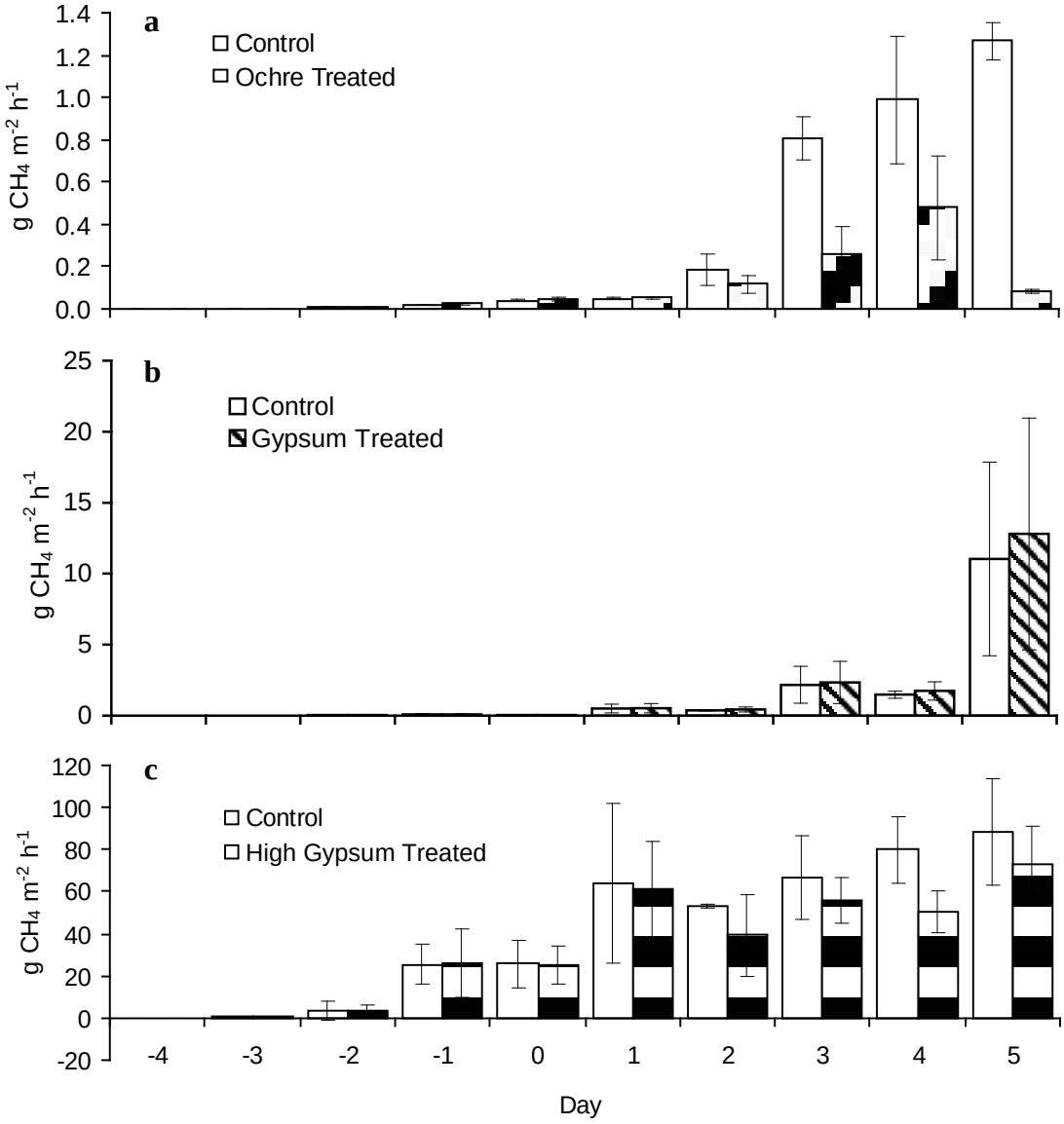

Fig. 3. Mean daily $CH_4$ fluxes (± standard error, n = 3 measurements per day) from pairs of sediment cores incubated at varying water temperature for (a) ochre and (b) gypsum treatment experiments. Negative days represent the acclimatisation period. Inhibitor application at 5 t $ha^{-1}$ to one of the cores occurred on Day 0 approximately 3 h before the first headspace $CH_4$ sampling. The different temperature ranges in the experiments were due to different field water temperatures when the cores were collected. After treatment the water temperature was normally increased by 5 $^{o}$C-steps every 48 h. In (a) $CH_4$ fluxes from Day -7 and Day -7 to -5 in the control

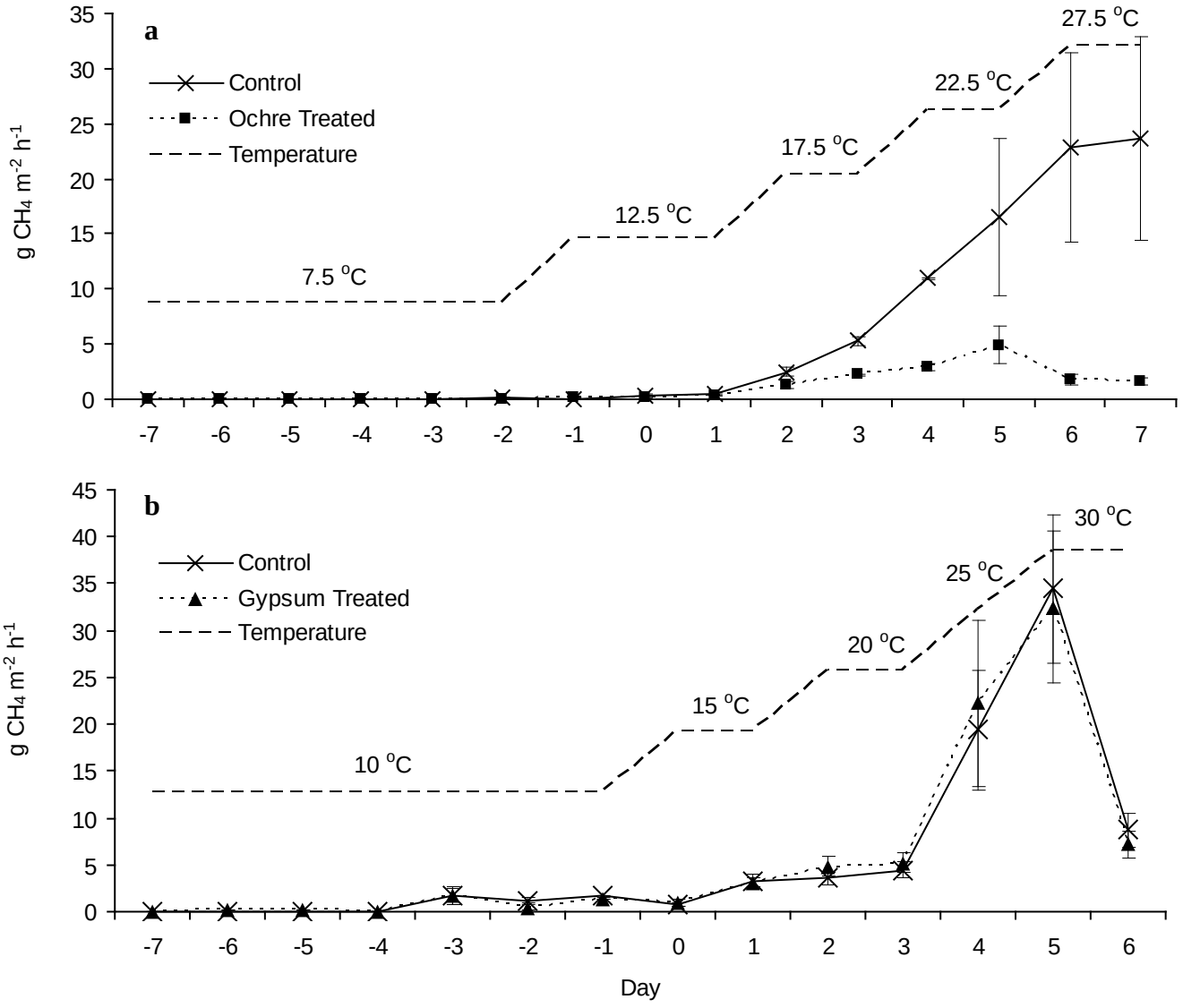

Table 1. Mean (n = 2-4) monthly % removal of $NO_3$ and $NH_4$ by the wetland calculated from the differences in concentration between water samples at the wetland inlets and outlet. Data for 2006 and 2007 are from van de Weg et al. (2008) and Reay and Paul (2008), respectively.

| | $NO_3$ | | | $NH_4$ | | |
|---|---|---|---|---|---|---|
| | 2006 | 2007 | 2008 | 2006 | 2007 | 2008 |
| January | - | - | -3 | - | - | 35 |
| February | 9 | 25 | 75 | 90 | -29 | 31 |
| March | 22 | 84 | 32 | 99 | 84 | 67 |
| April | 39 | 31 | 63 | 70 | 68 | 97 |
| May | 75 | 77 | 21 | 12 | 59 | 96 |
| June | 99 | 54 | 70 | 64 | 88 | 76 |
| July | - | - | 99 | - | - | 62 |

Table 2. $Q_{10}$ coefficients and best-fit $CH_4$ emission-water temperature relationships for the field experiment and the ochre and gypsum treatment sediment core experiments incubated at varying temperature in the laboratory.

| Temperature range | Control plot/core | | Treatment plot/core | |
|---|---|---|---|---|
| $^oC$ | $Q_{10}$ | Temperature relationship | $Q_{10}$ | Temperature relationship |
| | | Field experiment | | |
| 3.5-16.5 | 7.58 | Exponential ($R^2$ = 0.953, P=0.001) | 2.24 | Ochre: Exponential ($R^2$ = 0.831, P=0.011) |
| | | | 6.50 | Gypsum: Exponential ($R^2$ = 0.997, P<0.001) |
| | | Ochre laboratory experiment | | |
| 7.5-17.5 | 57.5 | Exponential ($R^2$ = 0.800, P=0.007) | 34.3 | Exponential ($R^2$ = 0.909, P=0.001) |
| 12.5-22.5 | 34.4 | Exponential ($R^2$ = 0.938, P=0.002) | 17.1 | Exponential ($R^2$ = 0.902, P=0.001) |
| 17.5-27.5 | 5.98 | Linear ($R^2$ = 0.951, P=0.001) | 0.948 | None ($R^2$ = 0.001, P=0.952) |
| | | Gypsum laboratory experiment | | |
| 10-20 | 2.82 | Linear ($R^2$ = 0.599, P=0.071) | 5.70 | Linear ($R^2$ = 0.817, P=0.013) |
| 15-25 | 9.55 | Exponential ($R^2$ = 0.764, P=0.053) | 11.3 | Exponential ($R^2$ = 0.865, P=0.022) |
| 20-30 | 5.36 | Exponential ($R^2$ = 0.581, P=0.134) | 3.94 | Exponential ($R^2$ = 0.404, P=0.250) |